Some peculiar features of plastic deformation and diffusion processes in hot extrusions of n-$Bi_2(Te, Se)_3$ and p-$(Bi, Sb)_2Te_3$

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Abstract

Extrusion is effected through conical dies, with high elongation ratio. It has been proved that in isobaric conditions the plastic deformation rate ($\dot{\varepsilon}$) and temperature (T) relation in $\lg\dot{\varepsilon}$ - 1/T coordinates is described by Arrhenius equation $\dot{\varepsilon} \approx \exp(-Q/RT)$, where Q is apparent energy of the activation of plastic deformation, R is the Rydberg constant. Q value changes from 1.45 eV (the zone of minimal rates) to 0.79 eV (zone of maximal rates). For the investigation of the peculiar features of diffusion a combined Bi_2Te_3 and Sb_2Te_3 cylinder-shaped billet was used with a flat boundary between two components going along the billet axis. Concentration curves characterizing Bi and Sb distribution in press residue and extruded rods were obtained with a help of the MS-46 ("Cameca") device. The proportional growth was proved of the diffusion coefficient (D) with the increase of the rate of plastic deformation: $D \sim \dot{\varepsilon}$.

1. Introduction

Extrusion is both a highly efficient method of forming and one of the novel engineering methods for substantial improvement of the mechanical strength of thermoelectric materials without any variation of their high thermoelectric figure of merit [1]. In conditions of commercial or full-scale manufacture of thermoelectric modules the application of the process of extrusion of materials based on solid solutions of antimony and bismuth chalcogenides will significantly enhance the throughput of the process of fabrication of highly efficient products. Therefore, the research into the process of extrusion of thermoelectric materials deserves the adequate attention. By present, the mechanizms of recrystallization, causes of the variation of thermoelectric properties after annealing have been identified, the relation has been found between the structure of deformation and the material behaviour during annealing. The post-extrusion and post-annealing crystallographic texture has been investigated [2]. However, insufficient attention was attached to the research into the issues, which are of great importance for extrusion technology application, such as, temperature and rate conditions of plastic deformations during hot extrusion, and diffusion processes in extrusion.

Plastic deformation of crystalline solids is always accompanied by the intensive initiation and migration of dislocations. In case with extrusion, the non-basic sliding of dislocations (migration of screw dislocations) results in the intensive formation of vacancies during their intersection [3]. In this case, due to continuous exchange of places between the vacancies and atoms of the material the balancing of the concentrations inside the thermoelectric material takes place, i.e., the process of self-diffusion, which rate is by several orders of magnitude higher than in case of conventional homogenizing annealing.

This allows the synthesis of alloys by method of mechanical fusion of parent elements in the process of hot extrusion [1]. The rate of the formation of vacancies is proportional both to the concentration of screw dislocations and to the rate of their migration, i.e. to the rate of plastic deformation accordingly. In this connection of great interest is the research into the effect of the rate of plastic deformation in extrusion on the diffusion balancing of concentrations.

2. Plastic deformation

2.1. Experiment and calculations

Plastic deformation was effected by method of hot extrusion through conical dies with elongation ratio k= 44.5; 64; 289 and 361. The elongation ratio was assumed as the relation of cross-sectional areas of the parent billet (F) and the extruded rod (f): k=F/f. Use was made of cylinder-shaped billets of a 16 mm diameter prepared by method of cold pressing of the powdered thermoelectric material of a n-$Bi_2Te_{2.7}Se_{0.3}$ composition and of a p-$Bi_{0.5}Sb_{1.5}Te_3$

composition. The average rate of plastic deformation for the deformation center was calculated by the following formula: $\dot{\varepsilon}=\varepsilon/t$, where ε is the extent of deformation, t is the time of deformation. The extent of deformation was calculated by the formula: $\varepsilon = \frac{F-f}{F}$. The time of deformation was calculated as the relation of the volume pressing center of deformation (B) to the volume of the material flowing out per second (B_s): $t=B/B_s$.

2.2. Isobaric conditions

With the fixed values of pressure (500 MPa, 800 MPa, 1,000 MPa) the temperature (T) dependence was found of the average rate of plastic deformation ($\dot{\varepsilon}$) for the center of deformation. In this case, the elongation ratio was k=289. In $\lg \dot{\varepsilon} - 1/T$ coordinates (Fig.1) the test points were on straight lines in compliance with Arrhenius equation: $\dot{\varepsilon} \sim \exp(-Q/RT)$, where Q was the apparent energy of the activation of the plastic deformation, R was the Rydberg constant. The results of calculation showed that in the zone of maximal rates the apparent energy of activation reached its maximum of 1.45 eV. With the medium rates the value of Q dramatically dropped to 0.79 eV.

2.3. Isothermal conditions

With the fixed values of temperature (400°C, 440°C, 450°C, 480°C) the deformation center average plastic deformation rate ($\dot{\varepsilon}$) dependence of pressure was found. The elongation ratio was k=289. In $\lg P - \lg \dot{\varepsilon}$ coordinates (Fig.2) the test points were on broken straight lines described by the equation $P=N \cdot \dot{\varepsilon}^m$, where N is a constant, m is the deformation-rate sensitivity index. From the changing slope of straight lines it follows that with the $\dot{\varepsilon}$ increase, *m* continuously decreases from ~0.8 (for the n-$Bi_2(Te, Se)_3$ material for $\leq 10^{-2}$ s^{-1} rates) to less than 0.2 (for maximum rates). Stepwise variation of the deformation-rate sensitivity index indicates the stepwise nature of the variation of the mechanism of plastic deformation with the variation of the rate of deformation during hot extrusion in isothermal conditions.

It should be mentioned that in a broad range of plastic deformation rates for n-$Bi_2(Te, Se)_3$ and p-$(Bi, Sb)_2Te_3$ rods extruded in isothermal conditions a relative stability of thermoelectric characteristics is observed (Fig. 3).

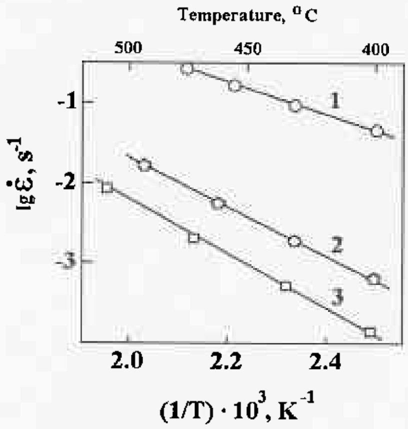

Fig.1. Temperature dependence of the n-$Bi_2(Te, Se)_3$ rate of plastic deformation for fixed pressure values 1 – 1,000 MPa; 2 – 800 MPa; 3 – 500 MPa. Elongation ratio k=289.

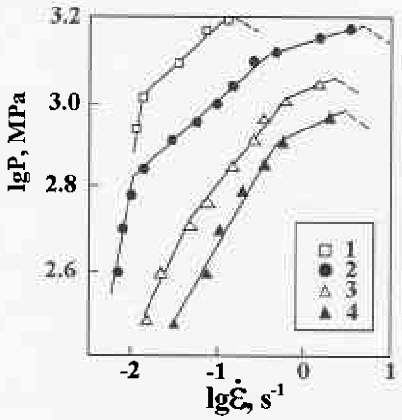

Fig. 2. Plastic deformation rate ($\dot{\varepsilon}$) dependence of pressure (P) for the fixed temperature values:
1 – 400°C [p-$(Bi, Sb)_2Te_3$];
2 – 440°C [n-$Bi_2(Te, Se)_3$];
3 – 450°C [p-$(Bi, Sb)_2Te_3$];
4 – 480°C [p-$(Bi, Sb)_2Te_3$].

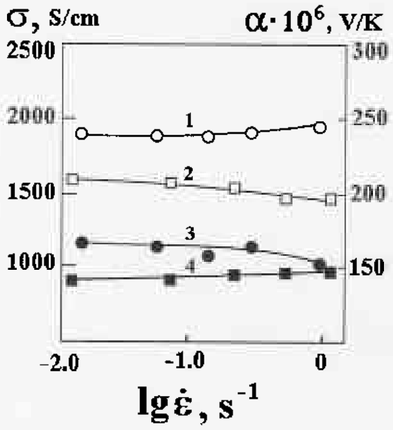

Fig. 3. Plastic deformation rate dependence of electrical conductivity (1, 2) and Seebeck coefficient (3, 4) of p-$(Bi, Sb)_2Te_3$ (1, 3) and n-$Bi_2(Te, Se)_3$ (2, 4) rods extruded at k=64.

3. Diffusion

3.1. Experiment and calculations

For the research into the laws governing the diffusion in plastic deformation the combined cylinder-shaped billets of a 16 mm diameter were used. They were prepared by way of cold pressing of briquettes made of powdered Sb_2Te_3 and Bi_2Te_3 thermoelectric materials. Briquettes were cut along the axis and then Sb_2Te_3 and Bi_2Te_3 half-briquettes formed an billet for the extrusion with a flat boundary going along the billet axis (Fig. 4).

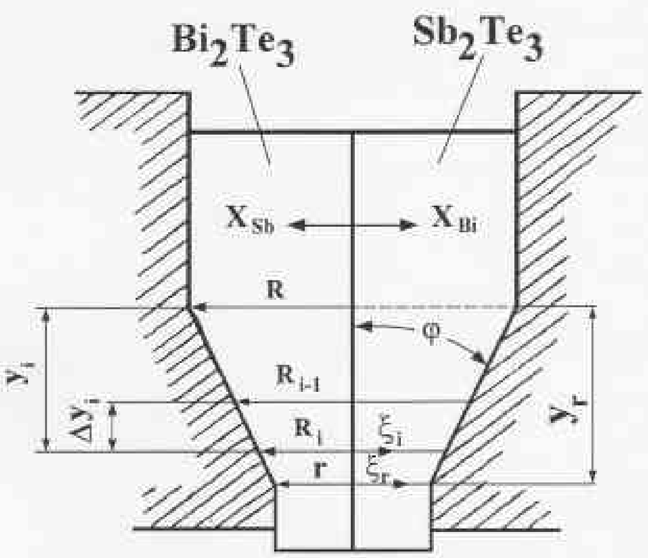

Fig. 4. Configuration of the binary Sb_2Te_3/Bi_2Te_3 billet for the research into Bi and Sb diffusion resulting from hot extrusion: $\xi_i = x_i \cdot R/R_i$ is the diffusion depth with due account for plastic deformations; x_i is the diffusion depth observed in experiment.

Research into diffusion was effected with transverse and longitudinal sections being perpendicular to the boundary between Sb_2Te_3 and Bi_2Te_3 materials.

Concentration curves characterizing Bi and Sb distribution in press residue and extruded rods were obtained with a help of the MS-46 ("Cameca") device. X-ray characteristic radiation of the elements was registered for Sb along the $L_{\alpha 1}$ line, for Bi – along the $M_{\alpha 1}$ line. The diameter of the electronic probe was 1 μ. Based on the concentration curves the depth of Sb penetration into Bi_2Te_3 and accordingly, that of Bi penetration into Sb_2Te_3 were calculated.

Calculations were made with the use of the Lyubov-Fastov equation [4] for diffusion in the environment affected by plastic deformations. In this case the boundary conditions determined by the tool geometry in extrusion were taken into account [5]. The derived solution of the diffusion equation allows the calculation of the D_i diffusion coefficient of the chemical element under consideration in any Δy_i layer affected by plastic deformation and located at a y_i distance from the original deformation point of the investigated Sb_2Te_3/Bi_2Te_3 system. It is as follows: $D_i = C_1 V \xi_i \cdot \Delta\xi_i/\Delta y_i$, where C_1 is the constant; V is the rate of the combined billet entering the zone of plastic deformation; $\xi_i = x_i \cdot R/R_i$ is the diffusion depth with due account for plastic deformation; x_i is the diffusant displacement observed in experiment; R is the billet radius before its entering the zone of plastic deformation; R_i is the billet radius in the zone of plastic deformation at a y_i distance from the original deformation point; $\Delta\xi_i$ is the displacement of the diffusant with the displacement of the billet layer in the zone of plastic deformation to a Δy_i distance.

3.2. Thermodynamics of diffusion

Before the parent combined billet entering the center of deformation (the pressing part of the die) in the process of extrusion, no plastic deformation is observed on the phase boundary of Sb_2Te_3/Bi_2Te_3. In these conditions the processes of interdiffusion of bismuth telluride and antimony telluride depends only on the variation of entropy (ΔS), variation of enthalpy (ΔH) and variation of isobaric-isothermal potential (ΔG) of the system [6]. Thermodynamic calculations were made based on the assumption that the zero concentration of the diffusing material correlates with the Sb_2Te_3/Bi_2Te_3 phase boundary, when the diffusion processes did not begin yet. Then, a series of concentration values of the diffusing material (0; 0.2; 0.4;…1 % mass) was set for the calculations and the thermodynamic parameters of the system were calculated. Fig. 5 shows their dependence on the diffusing material concentration at the extrusion temperature (700 K).

From the data of Fig. 5 it is clear that the process of bismuth telluride diffusion into antimony telluride is characterized by the negative variation (decrease) of entropy and enthalpy and by the positive variation of the isobaric-isothermal potential. Therefore, this process is not feasible in terms of thermodynamics, and it cannot go spontaneously. Diffusion of antimony telluride into bismuth telluride results in the positive variation (growth) of entropy and enthalpy, while the

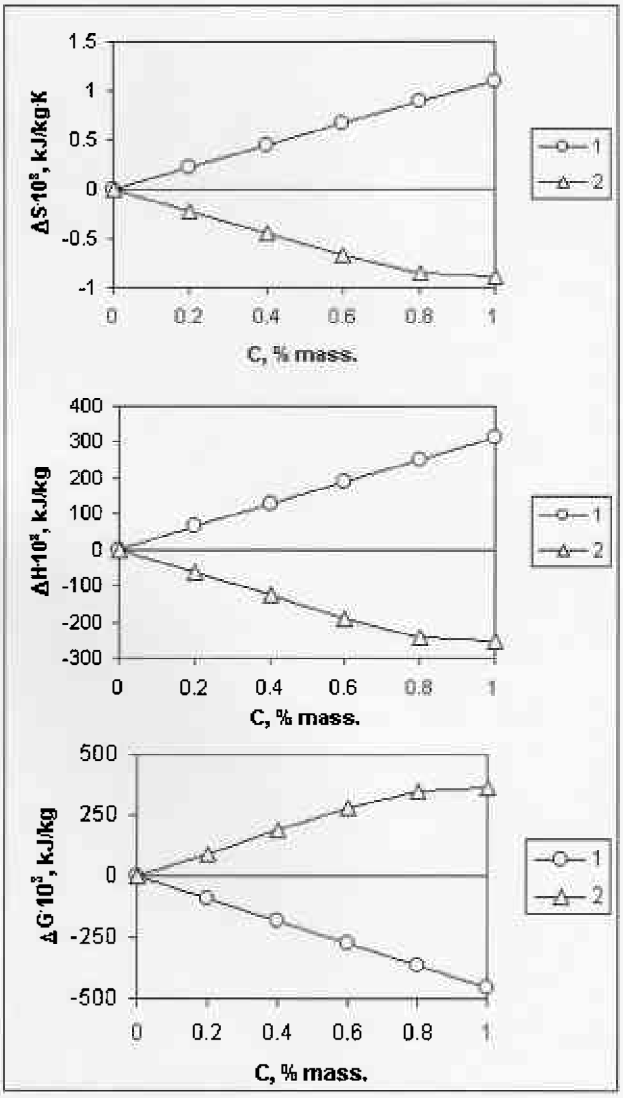

Fig. 5. Diffusing material concentration dependence of entropy (ΔS), enthalpy (ΔH) and isobaric-isothermal potential (ΔG): 1 – Sb_2Te_3; 2 – Bi_2Te_3.

variation of the isobaric-isothermal potential is negative. In this case, the process of diffusion goes spontaneously with the formation of $(Sb, Bi)_2Te_3$ solid solution. The entropy factor is the driving force of the process of Sb_2Te_3 dilution in the Bi_2Te_3 material.

3.3. Diffusion in rods

With rods produced by method of hot extrusion of combined billets (Fig. 4) the depth of Bi diffusion in Sb_2Te_3 and Sb diffusion in Bi_2Te_3 was investigated. It was found (see the Table below) that with the elongation ratio k=64 the variation of the rate of plastic deformation from 0.03 s^{-1} to 0.156 s^{-1} actually did not result in the variation of the depth of Bi and Sb penetration. For instance, its value for Bi was 158±2 μ, while for Sb it was 122 μ.

With elongation ratio k=361 and variation of the rate of deformation from 0.0065 s^{-1} to 1.55 s^{-1} the depth of Bi penetration was 198±15 μ, while that of Sb penetration was150±14 μ. The increase of the rate of deformation by nearly thousand times did not result in the thousandfold decrease of the depth of diffusion. Therefore, in this case, with a nearly thousandfold growth of the rate of deformation the diffusion coefficient also increases by thousand times. Thus, as it follows from the experiments, the diffusion coefficient is proportional to the rate of plastic deformation: $D_i \sim \dot{\varepsilon}$.

It should be noted also that with the increase of the elongation ratio the diffusion depth of the diffusant (Bi into Sb_2Te_3 and Sb into Bi_2Te_3) also grows. The identified proportional growth of the diffusion coefficient with the increase of the rate of plastic deformation in extrusion explains the relative stability of thermoelectric characteristics of extruded n-$Bi_2(Te, Se)_3$ and p-$(Bi, Sb)_2Te_3$ rods in a broad range of rates (Fig. 3).

As it is proved by the thermodynamic analysis, in the period of extrusion before the billet entering the zone of plastic deformation the diffusion of Sb in the Bi_2Te_3 compound is more probable than the diffusion of Bi in the Sb_2Te_3 compound, as it results in the growth of the system entropy (fig. 5). However, in the zone of plastic deformation the diffusion displacement of Bi in Sb_2Te_3 exceeds the diffusion displacement of Sb in Bi_2Te_3 (see the Table). It means that with the plastic deformation the formation of vacancies in the Sb_2Te_3 material goes more intensively than in the Bi_2Te_3 material. As a result of the exchange of places between the vacancies and atoms of the material, the balancing of the concentrations on the Sb_2Te_3/Bi_2Te_3 boundary will tend towards the higher density of vacancies.

3.4. Diffusion in press residue

Plastic deformation in extrusion predominantly takes place in the pressing part of the die (center of deformation). Investigation of a section of the press residue from the pressing part of the die with a small angle φ (Fig.4) showed that the dependence of Bi penetration into Sb_2Te_3 on the material migration route (y_i) in the center of deformation

Table. Difusion displacement of Bi and Sb in rods produced by method of hot extrusion of Sb_2Te_3/Bi_2Te_3 combined billets.

Tool geometry		Extrusion conditions			Bi diffusion in Sb_2Te_3		Sb diffusion in Bi_2Te_3	
k	y_r, mm	T, °C	P, MPa	$\dot{\varepsilon}$, s^{-1}	$\xi_r=x \cdot R/r$, μ	ξ_r mean, μ	$\xi_r=x \cdot R/r$, μ	ξ_r mean, μ
64	1.88	430	250	0.03	157	158±2	122	122
			500	0.156	160		122	
361	2.03	360	375	0.02	201	198±15	152	150±14
			1000	0.34	201		133	
		430	375	0.0065	213		167	
			625	0.078	171		160	
			875	0.82	217		156	
			900	1.55	190		129	
		470	375	0.16	201		137	
			575	0.69	209		167	
			675	0.87	179		152	

was approximated by the straight line: $\xi_i=C_2 \cdot y_i$ with a ±10% accuracy. (Fig. 6).

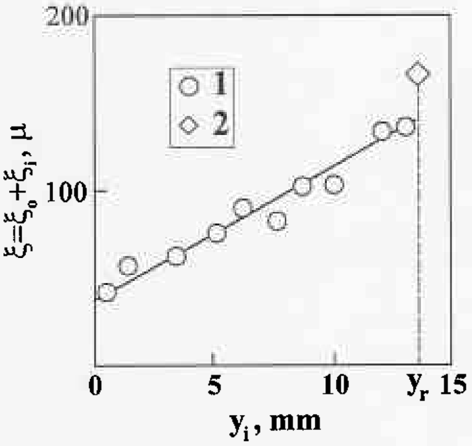

Fig. 6. Dependence of Bi penetration into Sb_2Te_3 on the material migration route length (y_i) in the center of deformation: 1 – according to the data of the press residue investigation (φ=30°; k=44.5) after extrusion at T=480°C and the rate of the billet entering the center of deformation V=0.5 mm/s; 2 – according to the data of the investigation of extruded rods.

Accordingly, $\Delta\xi_i=C_2\Delta y_i$. Then $D_i=CVy_i$, where $C=C_1C_2^2$. At the moment of leaving the deformation center $D_r=CVy_r$. As $V \sim \dot{\varepsilon}$, then $D_r \sim \dot{\varepsilon}$. Sufficiently high value of the diffusing element displacement at the original point of the deformation center ($y_i=0$) can be explained by the fact that the process of diffusion activation begins even before the material entering the geometric center of deformation.

The depth of Bi diffusion in Sb_2Te_3 in rods extruded with the use of dies with a great length of the deformation center (see Fig. 6, y_r=17.5 mm) is greater than in rods extruded with a short length of the center of deformation (see the Table, y_r=1.88 mm). This allows the conclusion that for the increase of the diffusion depth of the diffusant it seems feasible to increase the length of the center of deformation.

This point is particularly important for the design of dies intended for the extrusion of n-$Bi_2(Te, Se)_3$ and p-$(Bi, Sb)_2Te_3$ rods of a greater diameter, for instance, of a 30 mm diameter.

4. Conclusions

In isobaric conditions of extrusion, in the zone of minimal rates of plastic deformation the apparent energy of activation of n-$Bi_2(Te, Se)_3$ plastic deformation is maximal, and it reaches 1.45 eV. In the zone of medium rates of plastic deformation it decreases to 0.79 eV that indicates the variation of the mechanism of plastic deformation.

In case of isothermal conditions of extrusion the plastic deformation-rate sensitivity index of plastic deformation for the n-$Bi_2(Te, Se)_3$ material stepwise decreases from 0.8 eV at slow rates of plastic deformation to 0.2 eV at maximal rates of plastic deformation, i.e., a stepwise variation of the mechanism of plastic deformation takes place.

The proportional growth of the diffusion coefficient with the increase of the rate of plastic deformation was found.

For the activation of the diffusion processes in hot extrusion it seems feasible to reduce the angle of the die with a concurrent increase of the elongation ratio.

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